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Transport in Porous Media

A screening model for evaluating the degradation and transport of MTBE and other fuel oxygenates in the subsurface

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Abstract

Methyl *tert*-butyl ether (MTBE) has received high attention as it contributed to cleaner air and contaminated thousands of underground storage tank sites. Because MTBE is very water soluble, it is more difficult to remove from water by conventional remediation techniques. Therefore, biodegradation of MTBE has become a remediation alternative. In order to understand the transport and transformation processes, we present a closed form solution as a screening tool in this paper. The possible reaction pathways of first-order reactions are described as a reaction matrix. The singular value decomposition is conducted analytically to decouple the partial differential equations of the multi-species transport system coupled by the reaction matrix into multiple independent subsystems. Therefore, the complexity of mathematical description for the reactive transport system is significantly reduced and analytical solutions may be previously available or easily derived.

Key words: *solution, MTBE, reaction, degradation, transport, first-order decay.*

1. Introduction

Fuel oxygenates, such as methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), and di-isopropyl ether (DIPE), are used as gasoline additives to reduce air pollution. The frequent occurrence of leakage at fuel tank sites led the contamination of groundwater by those additives. Because of their high solubility in water (Fayolle *et al.*, 2003), it is more difficult to remove them from water by conventional remediation techniques (bioventing, activated carbon filtering, etc.). Instead, biodegradation of fuel oxygenates has caught a great attention (Happel *et al.*, 1998; Deeb *et al.*, 2000; Stocking *et al.*, 2000; Fiorenza and Rifai, 2003; Fayolle *et al.*, 2003; Schmidt *et al.*, 2004). Field studies of MTBE biodegradation have been summarized by Fiorenza and Rifai (2003). Large scale studies have been conducted for MTBE's fate and plume evolution in groundwater (Happel *et al.*, 1998; Buscheck *et al.*, 1998). In order to gain more insights into the transport and transformation of MTBE and other oxygenates at field scale, quantitative models are needed. Uddameri (2001) used a screening model (Jury *et al.*, 1983; Shoemaker *et al.*, 1990) for simulating MTBE (a single species) transport in vadose zone. However, laboratory-scale research indicates that the biodegradation of MTBE and other oxygenates produce daughter species and

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daughter species may further react to produce granddaughters (Church and Tratnyek, 2000). Single species transport models are unable to address daughter species' behavior.

Biodegradation pathways have been studied under various conditions (Church and Tratnyek, 2000; Stefan *et al.*, 2000). To the best of current knowledge, the possible pathway of MTBE and other oxygenates can be described as shown in Fig. 1. Although some reaction steps are hypothetical, the aerobic biodegradation of MTBE is demonstrable. Fig. 1 provides a preliminary picture of reaction networks to understand the coupled transport and transformation at field scale.

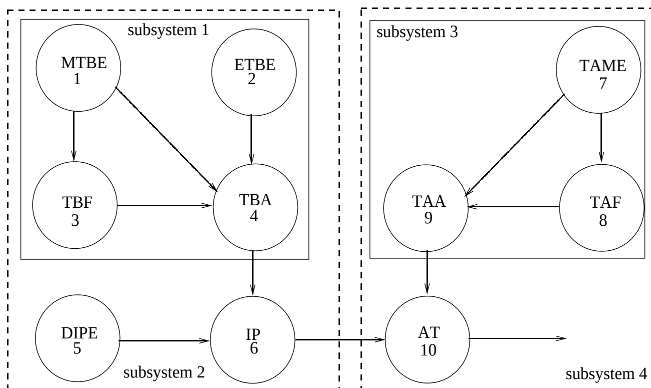

Figure 1. A possible pathway for complete degradation of MTBE and three other gasoline oxygenates (ETBE, TAME, and DIPE). MTBE=methyl *tert*-butyl ether, ETBE=ethyl *tert*-butyl ether, TAME=*tert*-amyl methyl ether, DIPE=di-isopropyl ether, TBA=*tert*-butyl alcohol, TAA=*tert*-amyl alcohol, TBF=*tert*-butyl formate, TAF = *tert*-amyl formate.

The transport equations coupled by such a reaction network are usually solved numerically. However, numerical methods are computationally expensive. Alternatively, analytical solutions are more suitable and practical for the preliminary evaluation of MTBE biodegradation and transport. In recent years, several authors used system decomposition techniques to simplify those partial differential equations coupled by first-order reactions and to derive analytical solutions (Sun *et al.*, 1999; Clement, 2001; Lu *et al.*, 2003). In this paper, we applied the singular value decomposition (SVD) analytically for the first-order reaction matrix and derived a closed-form solution for the transport and biodegradation of MTBE and other oxygenates in groundwater.

2. Mathematical Model and Solution Development

2.1 The Mathematical Model

The reactive transport system of Fig. 1 can be written as:

$$\frac{\partial \mathbf{c}}{\partial t} + \mathcal{L}(\mathbf{c}) = \mathbf{A}\mathbf{c}, \qquad \mathcal{L} = -D\frac{\partial^2}{\partial x^2} + v\frac{\partial}{\partial x}, \tag{1}$$

where $\mathbf{c}$ is the vector of concentrations $[ML^{-3}]$, which include, [MTBE], [ETBE], $\cdots$ as shown in Fig. 1, t is time $[T]$, D is the dispersion coefficient $[L^2T^{-1}]$, v is the constant groundwater velocity $[LT^{-1}]$, x is the coordinate in the direction of flow $[L]$, and $\mathbf{A}$ is the first-order reaction matrix and can be explicitly expressed as

$$\mathbf{A} = \begin{bmatrix} -k_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -k_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \alpha_1 k_1 & 0 & -k_3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \alpha_2 k_1 & k_2 & k_3 & -k_4 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -k_5 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & k_4 & k_5 & -k_6 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -k_7 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \beta_1 k_7 & -k_8 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \beta_2 k_7 & k_8 & -k_9 & 0 \\ 0 & 0 & 0 & 0 & 0 & k_6 & 0 & 0 & k_9 & -k_{10} \end{bmatrix}. \tag{2}$$

In matrix $\mathbf{A}$, α_1 and α_2 $(\alpha_1 + \alpha_2 = 1)$ are production fractions of TBF and TBA, respectively, from the degradation of MTBE, while β_1 and β_2 $(\beta_1 + \beta_2 = 1)$ are production fractions of TAF and TAA from the degradation of TAME.

2.2 System Decomposition

To solve Eq. (1), the singular value decomposition is conducted analytically. Since matrix $\mathbf{A}$ is diagonalizable, Eq. (1) can be expressed as

$$\frac{\partial \mathbf{c}}{\partial t} + \mathcal{L}(\mathbf{c}) = \mathbf{S}\mathbf{\Lambda}\mathbf{S}^{-1}\mathbf{c}. \tag{3}$$

where $\mathbf{\Lambda}$ is a diagonal matrix containing the eigenvalues of $\mathbf{A}$, and $\mathbf{S}$ is a matrix whose columns are linearly independent eigenvectors of $\mathbf{A}$. Multiplying by $\mathbf{S}^{-1}$, (3) becomes

$$\frac{\partial \mathbf{a}}{\partial t} + \mathcal{L}(\mathbf{a}) = \mathbf{\Lambda}\mathbf{a}, \qquad \mathbf{a} = \mathbf{S}^{-1}\mathbf{c}. \tag{4}$$

Each pde in (4) is independent of other pde's. Analytical solutions for (4) may be previously available or easily derived under various initial and boundary conditions.

The transform matrices are derived for the given system in Fig. 1 as:

$$\mathbf{S} = \begin{bmatrix} \frac{1}{k_1} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{k_2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{-\alpha_1}{k_1-k_3} & 0 & \frac{1}{k_3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \mathcal{S}_{4,1} & \frac{-1}{k_2-k_4} & \frac{-1}{k_3-k_4} & \frac{1}{k_4} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{k_5} & 0 & 0 & 0 & 0 & 0 \\ \mathcal{S}_{6,1} & \mathcal{S}_{6,2} & \mathcal{S}_{6,3} & \frac{-1}{k_4-k_6} & \frac{-1}{k_5-k_6} & \frac{1}{k_6} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{k_7} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{-\beta_1}{k_7-k_8} & \frac{1}{k_8} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \mathcal{S}_{9,7} & \frac{-1}{k_8-k_9} & \frac{1}{k_9} & 0 \\ \mathcal{S}_{10,1} & \mathcal{S}_{10,2} & \mathcal{S}_{10,3} & \mathcal{S}_{10,4} & \mathcal{S}_{10,5} & \frac{-1}{k_6-k_{10}} & \mathcal{S}_{10,7} & \mathcal{S}_{10,8} & \frac{-1}{k_9-k_{10}} & 1 \end{bmatrix}, \tag{5}$$

$$\mathcal{S}_{4,1} = \frac{1}{k_1 - k_4}\left(\frac{\alpha_1 k_3}{k_1 - k_3} - \alpha_2\right)$$

$$\mathcal{S}_{6,1} = \frac{-k_4\left[\alpha_1 k_3 - \alpha_2(k_1 - k_3)\right]}{(k_1 - k_3)(k_1 - k_4)(k_1 - k_6)} \qquad \mathcal{S}_{6,2} = \frac{k_4}{(k_2 - k_4)(k_2 - k_6)} \qquad \mathcal{S}_{6,3} = \frac{k_4}{(k_3 - k_4)(k_3 - k_6)}$$

$$\mathcal{S}_{9,7} = \frac{\beta_1 k_8 - \beta_2(k_7 - k_8)}{(k_7 - k_8)(k_7 - k_9)} \qquad \mathcal{S}_{10,1} = \frac{k_4 k_6\left[\alpha_1 k_3 - \alpha_2(k_1 - k_3)\right]}{(k_1 - k_3)(k_1 - k_4)(k_1 - k_6)(k_1 - k_{10})}$$

$$\mathcal{S}_{10,2} = \frac{-k_4 k_6}{(k_2 - k_4)(k_2 - k_6)(k_2 - k_{10})} \qquad \mathcal{S}_{10,3} = \frac{-k_4 k_6}{(k_3 - k_4)(k_3 - k_6)(k_3 - k_{10})}$$

$$\mathcal{S}_{10,4} = \frac{k_6}{(k_4 - k_6)(k_4 - k_{10})} \qquad \mathcal{S}_{10,5} = \frac{k_6}{(k_5 - k_6)(k_5 - k_{10})}$$

$$\mathcal{S}_{10,7} = \frac{-k_9 \left[\beta_1 k_8 - \beta_2 (k_7 - k_8)\right]}{(k_7 - k_8)(k_7 - k_9)(k_7 - k_{10})} \qquad \mathcal{S}_{10,8} = \frac{k_9}{(k_8 - k_9)(k_8 - k_{10})}$$

$$\mathbf{S}^{-} = \begin{bmatrix} k_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & k_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{\alpha_1 k_1 k_3}{k_1 - k_3} & 0 & k_3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \mathcal{S}^{-}_{4,1} & \frac{k_2 k_4}{k_2 - k_4} & \frac{k_3 k_4}{k_3 - k_4} & k_4 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & k_5 & 0 & 0 & 0 & 0 & 0 \\ \mathcal{S}^{-}_{6,1} & \mathcal{S}^{-}_{6,2} & \mathcal{S}^{-}_{6,3} & \frac{k_4 k_6}{k_4 - k_6} & \frac{k_5 k_6}{k_5 - k_6} & k_6 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & k_7 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{\beta_1 k_7 k_8}{k_7 - k_8} & k_8 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \mathcal{S}^{-}_{9,7} & \frac{k_8 k_9}{k_8 - k_9} & k_9 & 0 \\ \mathcal{S}^{-}_{10,1} & \mathcal{S}^{-}_{10,2} & \mathcal{S}^{-}_{10,3} & \mathcal{S}^{-}_{10,4} & \mathcal{S}^{-}_{10,5} & \frac{k_6}{k_6 - k_{10}} & \mathcal{S}^{-}_{10,7} & \mathcal{S}^{-}_{10,8} & \frac{k_9}{k9 - k_{10}} & 1 \end{bmatrix}, \qquad (6)$$

$$\mathcal{S}^{-}_{4,1} = \frac{k_1 k_4}{k_1 - k_4} \left(\frac{\alpha_1 k_3}{k_3 - k_4} + \alpha_2 \right)$$

$$\mathcal{S}^{-}_{6,1} = \frac{k_1 k_4 k_6 \left[\alpha_1 k_3 + \alpha_2 (k_3 - k_6)\right]}{(k_1 - k_6)(k_3 - k_6)(k_4 - k_6)} \qquad \mathcal{S}^{-}_{6,2} = \frac{k_2 k_4 k_6}{(k_2 - k_6)(k_4 - k_6)} \qquad \mathcal{S}^{-}_{6,3} = \frac{k_3 k_4 k_6}{(k_3 - k_6)(k_4 - k_6)}$$

$$\mathcal{S}^{-}_{9,7} = \frac{k_7 k_9 \left[\beta_1 k_8 + \beta_2 (k_8 - k_9)\right]}{(k_7 - k_9)(k_8 - k_9)} \qquad \mathcal{S}^{-}_{10,1} = \frac{k_1 k_4 k_6}{(k_1 - k_{10})(k_4 - k_{10})(k_6 - k_{10})} \left(\frac{\alpha_1 k_3}{k_3 - k_{10}} + \alpha_2 \right)$$

$$\mathcal{S}^{-}_{10,2} = \frac{k_2 k_4 k_6}{(k_2 - k_{10})(k_4 - k_{10})(k_6 - k_{10})} \qquad \mathcal{S}^{-}_{10,3} = \frac{k_3 k_4 k_6}{(k_3 - k_{10})(k_4 - k_{10})(k_6 - k_{10})}$$

$$\mathcal{S}^{-}_{10,4} = \frac{k_4 k_6}{(k_4 - k_{10})(k_6 - k_{10})} \qquad \mathcal{S}^{-}_{10,5} = \frac{k_5 k_6}{(k_5 - k_{10})(k_6 - k_{10})}$$

$$\mathcal{S}^{-}_{10,7} = \frac{k_7 k_9}{(k_7 - k_{10})(k_9 - k_{10})} \left(\frac{\beta_1 k_8}{k_8 - k_{10}} + \beta_2 \right) \qquad \mathcal{S}^{-}_{10,8} = \frac{k_8 k_9}{(k_8 - k_9)(k_9 - k_{10})}.$$

2.3 Sub-systems

The possible reaction network in Fig. 1 may be decomposed into subsystems. For example, if the subsystem for the first four species is considered, $\mathbf{S}$ and $\mathbf{S}^{-}$ matrices can be written

$$\mathbf{A}_1 = \begin{bmatrix} -k_1 & 0 & 0 & 0 \\ 0 & -k_2 & 0 & 0 \\ \alpha_1 k_1 & 0 & -k_3 & 0 \\ \alpha_2 k_1 & k_2 & k_3 & -k_4 \end{bmatrix}, \qquad (7)$$

$$\mathbf{S}_1 = \begin{bmatrix} \frac{1}{k_1} & 0 & 0 & 0 \\ 0 & \frac{1}{k_2} & 0 & 0 \\ \frac{-\alpha_1}{k_1 - k_3} & 0 & \frac{1}{k_3} & 0 \\ \frac{1}{k_1 - k_4} \left(\frac{\alpha_1 k_3}{k_1 - k_3} - \alpha_2 \right) & \frac{-1}{k_2 - k_4} & \frac{-1}{k_3 - k_4} & \frac{1}{k_4} \end{bmatrix}, \qquad (8)$$

$$\mathbf{S}_1^- = \begin{bmatrix} k_1 & 0 & 0 & 0 \\ 0 & k_2 & 0 & 0 \\ \frac{\alpha_1 k_1 k_3}{k_1 - k_3} & 0 & k_3 & 0 \\ \frac{k_1 k_4}{k_1 - k_4}\left(\frac{\alpha_1 k_3}{k_3 - k_4} + \alpha_2\right) & \frac{k_2 k_4}{k_2 - k_4} & \frac{k_3 k_4}{k_3 - k_4} & k_4 \end{bmatrix}. \tag{9}$$

If species 2 is not involved, the system transformation matrices can be simplified as

$$\mathbf{S}_1 = \begin{bmatrix} \frac{1}{k_1} & 0 & 0 \\ \frac{-\alpha_1}{k_1 - k_3} & \frac{1}{k_3} & 0 \\ \frac{1}{k_1 - k_4}\left(\frac{\alpha_1 k_3}{k_1 - k_3} - \alpha_2\right) & \frac{-1}{k_3 - k_4} & \frac{1}{k_4} \end{bmatrix}, \quad \mathbf{S}_1^- = \begin{bmatrix} k_1 & 0 & 0 \\ \frac{\alpha_1 k_1 k_3}{k_1 - k_3} & k_3 & 0 \\ \frac{k_1 k_4}{k_1 - k_4}\left(\frac{\alpha_1 k_3}{k_3 - k_4} + \alpha_2\right) & \frac{k_3 k_4}{k_3 - k_4} & k_4 \end{bmatrix}. \tag{10}$$

Substituting species 1, 3, 4 by species 7, 8, 9, the system transform equations (10) can be used for subsystem 3.

In the subsystem 1, if species 3 is not involved ($\alpha_1 = 0$ and $\alpha_2 = 1.0$, which means all MTBE reacts directly to produce TBA), the third column and third row in $\mathbf{A}_1$, $\mathbf{S}_1$ and $\mathbf{S}_1^-$ can be removed. Then,

$$\mathbf{A}_1 = \begin{bmatrix} -k_1 & 0 & 0 \\ 0 & -k_2 & 0 \\ k_1 & k_2 & -k_4 \end{bmatrix}, \quad \mathbf{S}_1 = \begin{bmatrix} \frac{1}{k_1} & 0 & 0 \\ 0 & \frac{1}{k_2} & 0 \\ \frac{-1}{k_1 - k_4} & \frac{-1}{k_2 - k_4} & \frac{1}{k_4} \end{bmatrix}, \quad \mathbf{S}_1^- = \begin{bmatrix} k_1 & 0 & 0 \\ 0 & k_2 & 0 \\ \frac{k_1 k_4}{k_1 - k_4} & \frac{k_2 k_4}{k_2 - k_4} & k_4 \end{bmatrix}. \tag{11}$$

2.4 A Solution

In the transformed domain, since each pde is independent, various analytical solutions can be used for "a" domain concentrations. For example, In a semi-infinite column, the solution of Bear (1979, p268) can be used,

$$a = \frac{a^o}{2} \exp\left(\frac{vx}{2D}\right) \left[\exp(-\mathcal{B}x)\mathrm{erfc}\gamma_i^- + \exp(\mathcal{B}x)\mathrm{erfc}\gamma_i^+\right], \tag{12}$$

where

$$\mathcal{B} = \left(\frac{v^2}{4D^2} + \frac{k}{D}\right)^{1/2}, \quad \mathrm{erfc}(\eta) = 1 - \mathrm{erf}(\eta) = \frac{2}{\sqrt{\pi}} \int_\eta^\infty \exp(-\tau^2) d\tau$$

$$\gamma^- = \frac{x - (v + 4kD)^{1/2} t}{2(Dt)^{1/2}}, \quad \gamma^+ = \frac{x + (v + 4kD)^{1/2} t}{2(Dt)^{1/2}}.$$

3. An Example

From extensive field data at the Borden aquifer site, Schirmer and Barker (1998) and Schirmer *et al.* (1999) calculated the first-order reaction rate (0.44 1/yr) for MTBE. Schirmer *et al.* (2003) further calibrated the reaction rates of MTBE and TBA (0.27 and 0.26 1/yr, respectively) from soil column studies. Although the derived solution is applicable for all ten species in Fig. 1, here we only demonstrate the solution of MTBE, TBF, and TBA in a semi-infinite domain. All concentrations are normalized by the boundary concentration of MTBE and system parameters are selected and assumed in Table 1.

Table 1. System parameters

velocity	v	0.4	$m\ d^{-1}$
dispersion coefficient	D	0.4	$m^2\ d^{-1}$
1st-order reaction rate MTBE	k_1	[0.44 0.27]	yr^{-1}
1st-order reaction rate TBF	k_3	0.30	yr^{-1}
1st-order reaction rate TBA	k_4	0.26	yr^{-1}
production fraction MTBE to TBF	α_1	0.7	
production fraction MTBE to TBA	α_2	0.3	

When the constant boundary concentration of MTBE is applied ($c_i^o = 0\ \forall i \neq 1$), Fig. 2 shows the close match between the analytical and numerical solutions and Fig. 3 shows the plume development of three species at four different times.

The beauty of analytical solutions is that sensitivity analyses in terms of system parameters can be done by using the closed form format of derivatives. For example, for two different reaction rates of MTBE given in Table 1, concentration sensitivities of all three species are shown in Fig. 4. It is arguable if MTBE reacts to produce TBA directly ($\alpha_1 = 0$ and $\alpha_2 = 1$) or indirectly through the intermediate product, TBF ($\alpha_1 = 1$ and $\alpha_2 = 0$). Using the solution derived, the concentration profiles for different combinations of direct and indirect reactions are calculated as shown in Fig. 5.

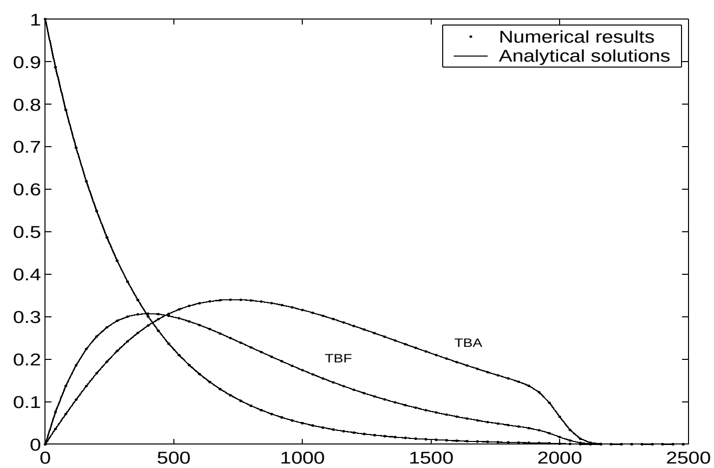

Figure 2. Comparison between analytical and numerical solutions for $k_1 = 0.44$ and $k_3 = 0.3$, $k_4 = 0.26$ 1/yr, and $t = 5000$ d.

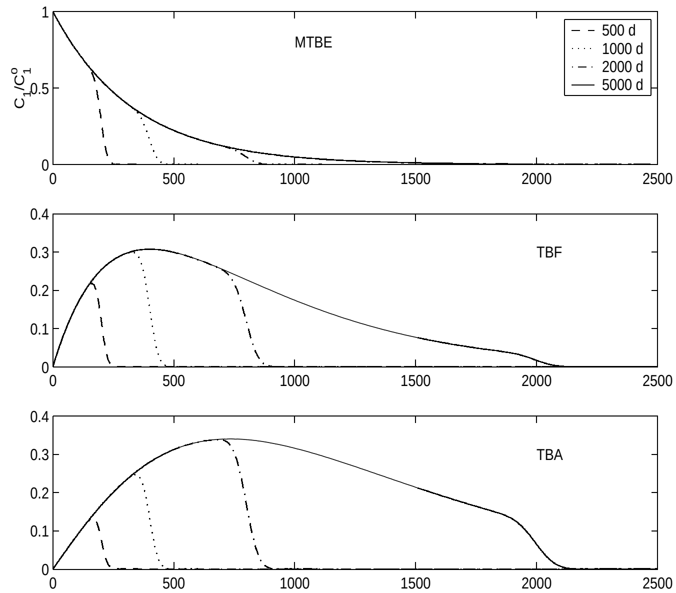

Figure 3. Concentration profiles of three species for four different times ($k_1 = 0.44$ and $k_3 = 0.3$, $k_4 = 0.26$ 1/yr).

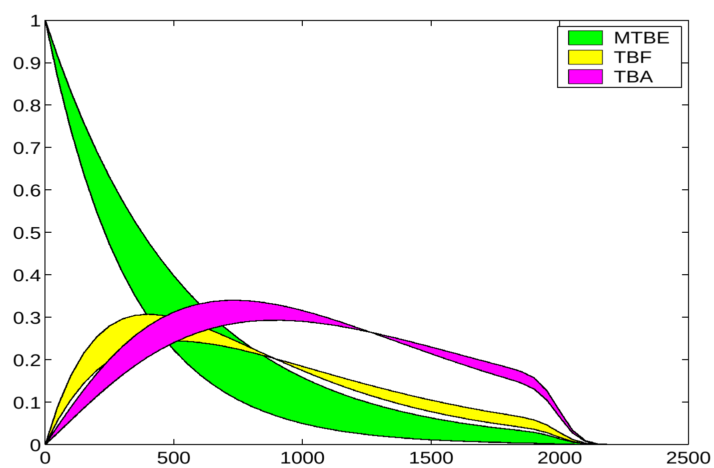

Figure 4. Concentration profiles for $k_1 \in [0.27\ 0.44]$ and $k_3 = 0.3$, $k_4 = 0.26$ 1/yr, and $t = 5000$ d.

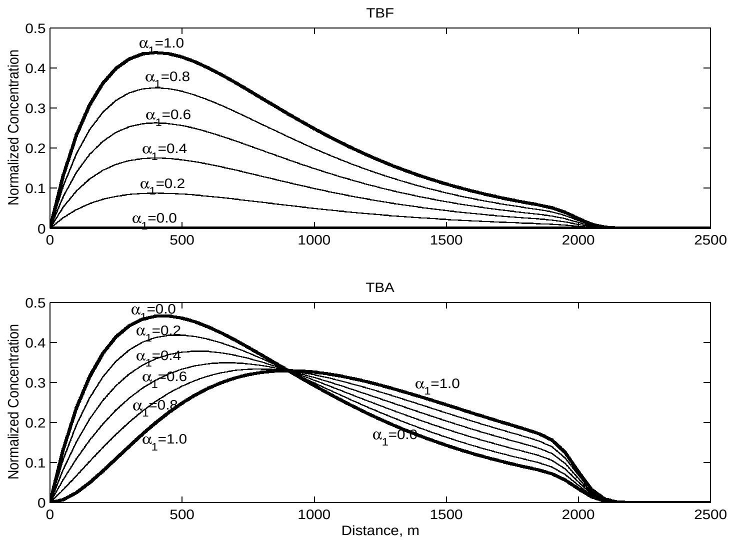

Figure 5. Concentration profiles of TBF and TBA for different α_1 values ($k_1 = 0.44$ and $k_3 = 0.3$, $k_4 = 0.26$ 1/yr, and $t = 5000$ d).

Conclusions

A closed form solution is presented for modeling the degradation and transport of MTBE and other oxygenates in the subsurface. A possible reaction network of MTBE (and other oxygenates) degradation is summarized and described as a matrix for a linear transport and reactive system. When the reactions are coupled in the partial differential equations, it is tedious and difficult (if it is not impossible) to derive closed form solutions using conventional integral transforms. Therefore, we demonstrate that the transport system coupled by MTBE degradation network can be decomposed into several simple systems by linear transformation. Analytical solutions may previously available or easily derived for those simple systems. The generalized transformation matrices ($\mathbf{S}$ and $\mathbf{S}^{-1}$) are provided for the given system in Fig. 1. For a real-world system, the transformation matrices for specific reactions can be further derived by simplifying the generalized matrices.

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